Thermodynamics of Cobalt (II, III) Oxide (Co₃O₄): Evidence of Phase Transition

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The Gibbs' energy change for the reaction, 3CoO (r.s.) + 1/2O₂(g) → Co₃O₄(sp), has been measured between 730 and 1250 K using a solid state galvanic cell: Pt, CuO + Cu₂O|(CaO)ZrO₂|CoO + Co₃O₄, Pt. The emf of this cell varies nonlinearly with temperature between 1075 and 1150 K, indicating a second or higher order phase transition in Co₃O₄ around 1120 (±20) K, associated with an entropy change of ~43 J mol⁻¹ K⁻¹. The phase transition is accompanied by an anomalous increase in lattice parameter and electrical conductivity. The cubic spinel structure is retained during the transition, which is caused by the change in Co³⁺ ions from low spin to high spin state. The octahedral site preference energy of Co³⁺ ion in the high spin state has been evaluated as -24.8 kJ mol⁻¹. The cation distribution therefore changes from normal to inverse side during the phase transition. The transformation is unique, coupling spin unpairing in Co³⁺ ion with cation rearrangement on the spinel lattice. DTA in pure oxygen revealed a small peak corresponding to the transition, which could be differentiated from the large peak due to decomposition. TGA showed that the stoichiometry of oxide is not significantly altered during the transition. The Gibbs' energy of formation of Co₃O₄ from CoO and O₂ below and above phase transition can be represented by the equations:

\[ 
\Delta G^0 = -205,685 + 170.79T(±200) \text{ J mol}^{-1}(730-1080 \text{ K}) 
\]

and

\[ 
\Delta G^0 = -157,235 + 127.53T(±200) \text{ J mol}^{-1}(1150-1250 \text{ K}). 
\]

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I. Introduction

The Gibbs' energy of formation of Co₃O₄ from CoO and O₂ has been measured by several investigators using manometric(1)-(5) and emf techniques(6)-(8). However, significant discrepancies still remain. The entropy change for the formation reaction obtained from dissociation pressure (or temperature) measurements(1)-(5) is numerically much smaller than that obtained from emf measurements(6)-(7). The third-law analysis of dissociation studies gives values for ΔH°₂₉₈ which show significant systematic dependence on the temperature of measurement. Although the emf measurements give better third-law values for ΔH°₂₉₈, their extrapolation to higher temperatures do not match the known decomposition temperatures in air or oxygen.

Cossee(9) has suggested that Co₃O₄ is a normal spinel in which Co³⁺ ions are in low spin state (t₄²). In most inorganic compounds Co³⁺ ion is in low spin configuration (e.g. ZnCo₂O₄(9), LiCoO₂(10)). However, Co³⁺ ions exist in high spin state (t₄²e²) in a few compounds such as Sr₂CoNbO₆, Sr₂CoSbO₆(10) and K₃CoF₆(11). Raccah and Goodenough(12) have shown that Co²⁺ ions exist in both low and high spin states in LaCoO₃ for T>648 K. A spin transition has been observed in Sr₂CoO₃ by Grenier et al.(13). Unpublished studies by the authors on thermodynamic properties of spinel solid solutions containing Co₃O₄ at 1200 K indicates that the ionic radius of Co³⁺ ion corresponds to high spin state. These observations suggest a possible spin unpairing in Co₃O₄. The Gibbs energy of formation of Co₃O₄ has therefore been redetermined

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in the temperature range 730 to 1250 K, spanning the full range of previous emf and dissociation studies. In addition TGA, DTA, X-ray diffraction and electrical conductivity measurements have been performed as a function of temperature to detect possible phase transitions.

II. Experimental Procedure

1. Materials

Fine powders of 99.99% pure cuprous oxide, cupric oxide and cobalt (II) oxide were obtained from Alfa Division of Ventron Corporation. Cobalt (II, III) oxide was prepared by heating cobalt (II) oxide in air at 1000 K. The argon gas, which was used to provide an inert atmosphere during emf measurements, was 99.99% pure. This was further dried over phosphorous pentoxide and deoxidized by passing over titanium granules at 1073 K. The calcia-stabilized zirconia solid electrolyte tube used in emf measurements was obtained from Corning Glass.

2. Apparatus and Procedure

The emf of the solid state cell,

\[ \text{Pt, CuO} + \text{Cu}_2\text{O}\left|(\text{CaO})\text{ZrO}_2\right|\text{CoO} + \text{Co}_3\text{O}_4, \text{Pt} \]

was measured as a function of temperature in the range 730–1250 K with a high impedance (>10^{12} \Omega) digital voltmeter. The reference and measuring electrodes were prepared by mixing the respective lower and higher oxides in the molar ratio of 1:2. The mixture of CoO and Co$_3$O$_4$ was compacted inside a calcia-stabilized zirconia tube with a Pt lead embedded in the mixture. The arrangement of the cell is shown schematically in Fig. 1. The calcia-stabilized zirconia tube was spring loaded against the reference electrode (CuO+Cu$_2$O), contained in a larger alumina tube, with a Pt mesh sandwiched between the two. The mesh was connected to a Pt lead. Prepurified Ar gas was used to flush both the zirconia tube and the alumina tube containing the reference electrode. The assembly was contained inside a vertical alumina tube, which in turn was suspended in a furnace such that electrodes were maintained in the constant temperature zone. Argon gas was passed through the outer alumina tube. An earthed stainless steel sheet wrapped around the outer alumina tube minimized induced voltage on Pt leads. The cell temperature was measured by a Pt/Pt-13%Rh thermocouple placed adjacent to the cell. The temperature of the cell was controlled to ±1 K.

The oxygen partial pressure above the electrodes became significant for \( T > 1000 \) K. The equilibrium was found to be disturbed by flowing Ar gas over the electrodes at these temperatures. To minimize the transpiration loss of oxygen, Ar flow was reduced to approximately \( 5 \times 10^{-8} \text{ m}^3\text{s}^{-1} (5 \times 10^{-2} \text{ mL s}^{-1}) \). At \( T > 1170 \) K, argon flow over the electrodes was stopped and the equilibrium oxygen partial pressures were established over the electrodes by the decomposition of the higher oxides. At temperatures below 1000 K Ar gas was flown at the rate of \( 1.5 \times 10^{-4} \text{ m}^3\text{s}^{-1} (1.5 \text{ mL s}^{-1}) \) on both electrodes. The reversibility of the cell was checked by passing small currents in either direction through the cell. In each case the emf
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returned to the original value before the titration. Reproducibility of the emf was checked by approaching the temperature from higher and lower values. The electrodes were examined after the experiment by X-ray diffraction, which showed that their phase composition was not altered during experiment.

A dc four probe method was used for measuring electrical conductivity of Co$_3$O$_4$. Low voltages (<200 mV) were applied during the conductivity measurements to prevent overheating of samples. The cylindrical samples for conductivity measurements were prepared from high purity cobalt (II) oxide, sintered at 1800 K in air for ~40 ks to a relative density of 85%. Platinum paste electrode and Pt wire connectors were attached to the pellet and the assembly was baked at 1200 K in oxygen for ~2 ks. The sample was heat treated in oxygen at 1000 K for ~100 ks to convert CoO to Co$_3$O$_4$. Completeness of conversion was verified by X-ray diffraction. Conductivity was measured from 720–1205 K.

The lattice parameter of Co$_3$O$_4$ was measured from room temperature to 1300 K in pure oxygen using a X-ray diffractometer equipped with high temperature furnace. For measurement at 1300 K oxygen was maintained at a pressure of $3 \times 10^5$ Pa. Temperature of the sample was measured to ±4 K. DTA and TGA experiments were done on pure Co$_3$O$_4$ at a scanning rate of 2°/min in air and oxygen at 1.01 × $10^5$ Pa.

### III. Results

The variation in emf of the cell with temperature is shown in Fig. 2. The emf varies nonlinearly between 1075 and 1150 K, indicating a possible phase transformation in one of the oxide phases present at the electrodes. The linear segments below and above this range can be represented by the equations:

$$E = -389.9 + 0.398 \ T(\pm 0.5) \quad \text{mV(730–1150 K)}$$

and

$$E = -138.9 + 0.174 \ T(\pm 0.5) \quad \text{mV(1130–1230 K).}$$

The oxygen potential of reference mixture of CuO and Cu$_2$O is given by $\mu_{O_2}$

$$\Delta \mu_{O_2} = -260,890 + 187.82 \ T(\pm 400) \ \text{J mol}^{-1}.$$  

The standard Gibbs' energy of formation of Co$_3$O$_4$ according to the reaction,

$$3\text{CoO(r.s.)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Co}_3\text{O}_4(sp)$$

computed from the emf are:

$$\Delta G_{(4)}^0 = -205,685 + 170.79 \ T(\pm 200) \ \text{J mol}^{-1}$$

(730–1100 K)

and

$$\Delta G_{(4)}^0 = -157,235 + 127.53 \ T(\pm 200) \ \text{J mol}^{-1}$$

(1130–1230 K).

The results of thermogravimetric analysis (TGA) shown in Fig. 3 indicate that the stoichiometry of Co$_3$O$_4$ remains unchanged until decomposition. Decomposition temperatures from TGA are 1173 (±2) K in air and 1233 (±2) K in pure oxygen at 1.01 × $10^5$ Pa. The decomposition temperature in air is in excellent agreement with the value of 1170 (±5) K measured by Sreedharan et al. (7). Differential thermal analysis (DTA) in air at the scanning rate of 2°/min shows the onset of an endothermic process starting at ~970 K and culminating on the main peak due to decomposition. The phase transition appears as a broad shoulder on the decomposition peak. A better separation of the thermal effects due to
phase transformation and decomposition was achieved by conducting DTA in pure oxygen as shown in Fig. 3. The broad endothermic peak corresponding to the phase transition appears to be composed of two subpeaks. The position of broad peak is different during heating and cooling, suggesting some hysteresis. The decomposition temperature is well delineated at 1233 K during both heating and cooling processes.

The variation of lattice parameter with temperature is shown in Fig. 4. Lattice parameter varies linearly with temperature up to approximately 900 K above which there is an anomalous increase. The cubic spinel structure is retained throughout the temperature range. The results of the present study are in fair agreement with the data of Touzelin(15) obtained in air and oxygen. The variation of the logarithm of the electrical conductivity of Co₃O₄ in pure oxygen is shown as a function of the reciprocal of absolute temperature in Fig. 5. The electrical conductivity follows
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Arrhenius type of relation upto 970 K above which there is an anomalous increase in conductivity.

IV. Discussion

The Gibbs’ energy change for the formation of Co₃O₄ from CoO and O₂ is compared in Figs. 6 and 7 with data available in the literature(1)-(8). Figure 6 compares the results over the entire temperature range covered in this study, whereas Fig. 7 displays a magnified picture of the high temperature region. The Gibbs’ energy change for the reaction (4) obtained by different investigators seems to agree closely (±1 kJ mol⁻¹) at 1130 K, although the slopes of the lines differ. Results obtained in this study between 730 and 1080 K are in good agreement with the results of Bugden and Pratt(6). The data of Sreedharan et al.(7) agree well at the higher temperatures but are more negative by 3 kJ mol⁻¹ than the results obtained in this study at 730 K. Measurements of Enoki et al.(8) agree exactly with the present measurements at 870 K but are more negative by 3.6 kJ mol⁻¹ at 1060 K.

The Gibbs’ energy of formation of Co₃O₄ obtained in present study in the temperature range 1130–1250 K are in excellent agreement with the measurements of Roiter and Paladino(3), Ingraham(4) and Aukrust and Muan(5). The values of Foote and Smith(1) are more negative by 0.4 to 1.0 kJ mol⁻¹. More recent studies of Oppermann et al.(2) are more positive by 1.5 to 2.0 kJ mol⁻¹.

A more precise indicator of temperature dependent errors in free energy measurements is provided by the third-law analysis. The enthalpy change for the reaction (4) at 298 K can be computed from free energy change at each temperature using the relation;

\[ \Delta H_{\text{298}}^{0} = \Delta G_{\text{298}}^{0} - T \Delta \phi \]  

where

\[ \phi = \frac{G_{\text{298}}^{0} - H_{\text{298}}^{0}}{T} \]

\[ = -S_{\text{298}}^{0} \int_{298}^{T} \frac{C_{P}^{0}}{T} \, dT + \frac{1}{T} \int_{298}^{T} C_{P}^{0} \, dT. \]  

The free energy functions (\( \phi \)) for CoO₄, CoO and O₂ are given in Janaf tables(16)(17). The free energy function for Co₃O₄ was calculated from heat capacity data of King(18) (54–296 K) and King and Christensen(19) (300–1000 K). Roth(20) has observed maximum magnetic susceptibility at 40 K for Co₃O₄. Mossbauer studies of Kundig et al.(21) indicate a Neel temperature

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**Fig. 6** Comparison of the Gibbs’ energy of formation of Co₃O₄ from CoO and O₂ as a function of temperature.

**Fig. 7** A magnified view of the temperature dependence of Gibbs’ energy of formation of Co₃O₄ in the vicinity of the transition temperature.
of 33 (±1) K. This transition is associated with antiferromagnetic ordering of Co^{+2} spin moments on tetrahedral sites. Therefore Janaf tables(16) have added a magnetic entropy contribution of 11.5 J mol^{-1} K^{-1} to that calculated from heat capacity data. The values of $\Delta H^0_{298}$ for the reaction (4) computed from free energy measurements below 1050 K are shown in Fig. 8 as a function of temperature of each free energy measurement. It is seen that $\Delta H^0_{298}$ computed from the results of Bugden and Pratt(6), Sreedharan et al.(7) and Enoki et al.(8) are strongly temperature dependent suggesting systematic temperature dependent errors in emf data. The values calculated from the results of this study are almost independent of temperature with the mean value of $\Delta H^0_{298} = -196.6 (±0.04) \text{kJ mol}^{-1}$. Since the phase transition detected in Co$_3$O$_4$ in this study has not been considered in the evaluation of free energy functions given in Janaf tables(16), they are not accurate for $T>1050$ K. Computation of accurate free energy function above 1000 K must await careful measurement of heat capacity of Co$_3$O$_4$ above this temperature. Reliance on extrapolated heat capacity data from low temperature is the main reason for the discrepancies in the third-law analysis of decomposition pressure (or temperature) measurements. A recent third-law analysis(22) of literature data on Gibbs’ energy of formation of Co$_3$O$_4$ obtained from emf studies uses older free energy functions for Co$_3$O$_4$ which do not include the magnetic contribution to entropy. The standard enthalpy of formation of Co$_3$O$_4$ from elements at 298 K derived from third-law analysis of present data and corresponding value for CoO(16) is $-911 (±1.3) \text{kJ mol}^{-1}$.

The emf, DTA, lattice parameter and conductivity measurements taken together indicate a second or higher order phase transition in Co$_3$O$_4$ extending from about 970 K to 1200 K. A transition temperature of 1120 (±20) K is obtained by extrapolating the linear segments of the emf (Fig. 2). This temperature also corresponds to the maximum slope on the conductivity plot (Fig. 5). However, maximum change in lattice parameter with temperature occurs at 1180 K. This phase transition is most probably due to a change in spin configuration of Co$^{+3}$ ion. The supporting evidence for this hypothesis comes from the fact that changes in the experimental lattice parameter and entropy accompanying the phase transition can be adequately explained on this basis.

The octahedral site preference energy of Co$^{+2}$ ion is $-32.9 \text{kJ mol}^{-1}$(23). The corresponding value of Co$^{+3}$ has been incorrectly calculated by McClure(24) as $-79.5 \text{kJ mol}^{-1}$. Recalculation based on [Dq]$_{oct}$ of 1755 cm$^{-1}$ for hydrated ion gives a value of $-396.9 \text{kJ mol}^{-1}$, corrected for oxygen ligand. Drago(25) has suggested a possibility of high spin state of Co$^{+3}$ ion in an octahedral environment of H$_2$O ligand with [Dq]$_{oct}$ of 1820 cm$^{-1}$. For the high spin state of Co$^{+3}$ the octahedral site preference energy is calculated as $-24.8 \text{kJ mol}^{-1}$. These values suggest that at lower temperature, where Co$^{+3}$ ion is in low spin state, Co$_3$O$_4$ would be a normal spinel with divalent cation in tetrahedral site and both trivalent cations in octahedral positions. When Co$^{+3}$ ion exists in high spin state, Co$_3$O$_4$ would change from the normal configuration to the inverse side. The exact cation distribution can be computed using the procedure of Jacob and
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Alcock$^{(20)}$. For the ion exchange reaction,

$$(\text{Co}^{+2}+\text{[Co}^{+3}]_{\text{HS}} \longrightarrow \text{(Co}^{+3})_{\text{HS}}+\text{[Co}^{+2}]\quad (9)$$

$$\Delta H^{m} = H_{\text{Co}^{+2}+\text{[Co}^{+3}]_{\text{HS}}} - H_{\text{Co}^{+3}+\text{[Co}^{+2}]_{\text{HS}}},$$

$$= -RT \ln \frac{(N_{\text{Co}^{+2}}) \cdot [N_{\text{Co}^{+3}}]}{(N_{\text{Co}^{+3}}) \cdot [N_{\text{Co}^{+2}}]}.$$. (10)

The cation distribution computed at 1200 K is

$$(\text{Co}^{+2})_{0.22} \cdot \text{Co}^{+3}_{0.78} \cdot \text{[Co}^{+2}]_{0.78} \cdot \text{[Co}^{+3}]_{0.22} \cdot \text{O}_4.$$ (11)

The lattice parameter of Co$_3$O$_4$ at temperatures below and above the transition temperature can be computed from the cation distribution and ionic radii of Co$^{+2}$, Co$^{+3}$ and O$^{-2}$ by solving the simultaneous equations:

$$R_{\text{tet}} = a \sqrt{3}(u-0.125)$$

and

$$R_{\text{oct}} = a(3u^2-2u+0.375)^{1/2}$$

where

$$R_{\text{tet}} = R_{\text{tet},A}(x) + R_{\text{tet},B}(1-x)$$

and

$$R_{\text{oct}} = R_{\text{oct},A}(0.5(1-x)) + R_{\text{oct},B}(0.5(1+x))$$

for the spinel AB$_2$O$_4$ having the cation distribution represented by $(A_xB_{1-x})[A_{1-x}B_{1+x}]O_4$. The ionic radii of Co$^{+2}$ ion are 0.058 and 0.0745 nm in tetrahedral and octahedral sites$^{(27)}$. The ion is present in high spin state on both sites at all temperatures. The Co$^{+3}$ ion on the tetrahedral site can only be present in high spin configuration because $\Delta_0$ is much smaller than $\Delta_0$ and therefore much less than pairing energy. The ionic radii of Co$^{+3}$ ion in octahedral environment in the low spin state is taken from Shannon and Prewitt$^{(27)}$, while that for the high spin condition is from Blasse$^{(10)}$. The calculated lattice parameter of Co$_3$O$_4$ corresponding to the normal spinel configuration with Co$^{+3}$ ion in low spin state is 0.813 nm. The value of lattice parameter based on the calculated cation distribution and Co$^{+3}$ ion in high spin state is 0.83 nm at room temperature. The difference of 0.017 nm at room temperature is close to the observed value of 0.0114 nm at 1300 K (Fig. 4).

The entropy change for the phase transition in Co$_3$O$_4$ calculated from the change in the temperature coefficient of the emf is 43.2 $(\pm 3)$ J mol$^{-1}$K$^{-1}$. There are three contributions to the entropy change for the transition. The first is configurational in origin resulting from cation mixing in the tetrahedral and octahedral sites of the spinel lattice above the transition temperature$^{(26)}$. From the cation distribution at 1200 K, the ideal entropy contribution is 15.5 J mol$^{-1}$K$^{-1}$ per mole of Co$_3$O$_4$. The second contribution is the electronic entropy accompanying the low spin to high spin transition in Co$^{+3}$. This contribution in $R \ln 3$ per Co$^{+3}$ ion or 18.3 J mol$^{-1}$K$^{-1}$ per mole of Co$_3$O$_4$. The third contribution is due to the increase in molar volume, which can be estimated using the relation,

$$\Delta S' = \gamma CV \frac{\Delta V}{V}$$

where $\Delta V$ is the volume change, $\gamma$ is the Grüneisen parameter, which ranges from 1 to 2, and $CV$ is the heat capacity at constant volume. The value of $(\Delta V/V)$ is 0.041 from lattice parameter measurements and $CV$ can be approximated by the ideal value of $3nR$ at high temperatures. The value of $\Delta S'$ for the transition ranges from 7.16 to 14.32 J mol$^{-1}$K$^{-1}$ depending on the value chosen for $\gamma$. An average value of 10.74 J mol$^{-1}$K$^{-1}$ can be taken as an estimate. The sum of the three contributions is 44.54 J mol$^{-1}$K$^{-1}$, in excellent agreement with the value of 43.2 $(\pm 3)$ J mol$^{-1}$K$^{-1}$ obtained from the emf measurement.

The coexistence of the two spin states probably occurs over a wide range of temperature. This is accompanied by change in cation distribution. The transition is therefore not of first order. This fits in with continuous change in emf, lattice parameter and electrical conductivity over a temperature range. It would be interesting to measure magnetic properties of Co$_3$O$_4$ as a function of temperature to confirm the hypothesis of spin transition and cation rearrangement.

V. Conclusion

The apparent discrepancy in thermodynamic properties of Co$_3$O$_4$ has been resolved by the detection of a new phase transition which couples a change in spin configuration of Co$^{+3}$
ions on octahedral site with cation rearrangement. For complete thermodynamic characterization of $\text{Co}_3\text{O}_4$, it is necessary to measure accurately heat capacities from 1000 K to the decomposition temperature.

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